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THE LASL THERMOCHEMICAL HYDROGEN PROGRAM
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Abstract

The LASL Hydrogen Program is continuing its investigation of practical schemes to decompose water thermochemically for hydrogen production. Efforts were and are being devoted to process improvements in cycles that use sulfuric acid as an intermediate. Sulfuric acid-hydrogen bromide cycles are being studied as a means of overcoming the heat penalty in drying acid solutions. An alternate approach involves the use of insoluble bismuth sulfate that is precipitated from acid solution.

Preliminary energy balances indicate a significant increase in cycle efficiency for both these options.

Introduction

In the development of practical thermochemical cycles for hydrogen production from water, the approach adopted by the Los Alamos Scientific Laboratory has been to verify proposed cycle reaction schemes by experiment. This verification involves the careful determination of yields, rates and equilibria as well as the thermochemistry of the individual reactions in a cycle under a wide variety of operating conditions. After demonstration of a cycle's scientific feasibility, a preliminary engineering analysis is attempted to evaluate cycle efficiency and cost. Further experimentation is carried out to optimize the cycle as indicated by the above analysis. Typically, enhanced reaction yield leads to lower internal recycle rates and thus to a smaller energy expenditure involved in the separation of reaction products. Increase in reaction velocity lessens residence times within a reactor and thus contributes to lower capital cost for the overall cycle.

If a cycle should appear promising after the initial evaluation described, a final phase of process development would involve a bench-scale, closed loop test that provides data for more realistic engineering evaluation and cost analyses.

Together with these activities, an attempt is being made to match the heat requirements of the cycle to potential heat sources which could be derived from either fission, fusion or solar energy.

Much of the work done in the LASL program has been described by members of the hydrogen group in both publications and presentations at national and international scientific meetings.(1-7) The program was also recently summarized at the Thermochemical Hydrogen Contractors' Review Meeting held at DOE-HQ in October.(6)

The process development and engineering analysis activities have been directed primarily to experimental studies of reactions relevant to cycles employing sulfuric acid as an intermediate substance. These cycles include the sulfuric acid-hydrogen bromide cycle, the hybrid sulfuric acid cycle (Westinghouse) and the sulfuric-acid-iodine cycle (General Atomic). The rationale for this work is to avoid the large heat penalties incurred on drying sulfuric acid solutions. The approach taken in the case of sulfuric acid-hydrogen bromide cycle has been to devise means of decomposing anhydrous hydrogen bromide which is produced with essentially pure sulfuric acid in one of the cycle steps making water evaporation unnecessary. In the work supporting the development of the hybrid cycle and the iodine cycle, the approach is slightly different. The use of an insoluble, non-hydrated, metal sulfate precipitated from sulfuric acid solutions as a means of recovering sulfur trioxide (and hence sulfur dioxide) without having to dry the acid is being continued. Efforts have been devoted to the engineering design and analysis of these modifications which produce smaller heat penalties as compared to the existing forms of the cycles. Results are an expected increase in cycle efficiency.

A preliminary view of cycles having maximum reaction temperatures in the 1500-1700 K range is being undertaken. These temperatures may be attained in magnetic fusion energy schemes. Magnetic fusion energy may thus incorporate thermochemical cycles in the production of synthetic fuels.
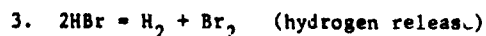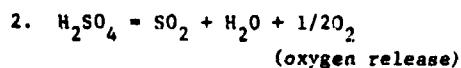
The Sulfuric Acid-Hydrogen Bromide Cycle

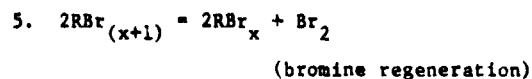The conceptual cycle can be best described by the following reactions:

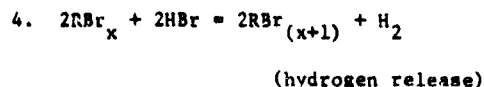Low Temperature Heat-Rejecting Reactions

1. $2H_2O + SO_2 + Br_2 = H_2SO_4 + 2HBr$

(water absorption)
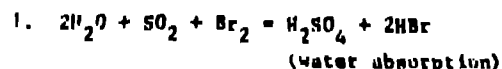
High Temperature Heat Absorbing Reactions

2. $H_2SO_4 = SO_2 + H_2O + 1/2O_2$

   (oxygen release)

3. $2HBr = H_2 + Br_2$ (hydrogen release)

In practice, as reaction 3 does not proceed as written except electrochemically, it is usual to substitute the following sequence.

4. $2RBr_x + 2HBr = 2RBr_{(x+1)} + H_2$

   (hydrogen release)

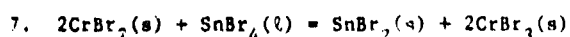5. $2RBr_{(x+1)} = 2RBr_x + Br_2$

   (bromine regeneration)

In principle, this cycle could be more efficient than the other sulfuric acid cycles under consideration. Reaction 1 yields nearly 100% H_2SO_4 rather than 50% H_2SO_4 as formed in the other cycles. Thus the rather large heat requirements for drying sulfuric acid can be avoided. In addition, typical ΔS^0 values for metal bromide decompositions are very near the value required for an "ideal" two-step decomposition of hydrogen bromide.
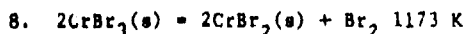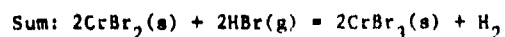
A preliminary energy balance illustrates this point further. This balance is shown in Table I. The products of reaction 1 are H_2SO_4 (liq.) and anhydrous HBr, the ΔH^0 for HBr decomposition is +72.8 kJ (for 2 mols of HBr), however the ΔG^0 for this reaction is +107.1 kJ. As Table II indicates, it is possible to use twice or three times the theoretical heat (of reaction) in a sulfuric acid-hydrogen bromide cycle and still obtain a thermal efficiency of the order of 50%.

From literature data, the VBr_2-VBr_3 couple and the $CrBr_2$-$CrBr_3$ couple have ΔG^0 values near the value required for the efficient decomposition of HBr. However, in both cases the reaction of HBr with the lower bromide (to evolve H_2) is far too slow.

Earlier, satisfactory reaction rates were demonstrated for reactions involving chromium bromide hydrates (3). Consequently, in an attempt to promote the chromium bromide reactions in the absence of water, reactions 6 and 7 of the following sequence were investigated.
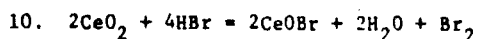
6. $SnBr_2(s) + 2HBr(g) = SnBr_4(\ell) + H_2$ 300-510 K

7. $2CrBr_2(s) + SnBr_4(\ell) = SnBr_2(s) + 2CrBr_3(s)$

   300-590 K

   Sum: $2CrBr_2(s) + 2HBr(g) = 2CrBr_3(s) + H_2$

8. $2CrBr_3(s) = 2CrBr_2(s) + Br_2$ 1173 K

The thermochemical properties of the $SnBr_2$-$SnBr_4$ couple would permit it to act as an oxidation-reduction catalyst to achieve the summation reaction. Reactions of HBr with mixtures containing known amounts of $SnBr_2$, $CrBr_2$, and $CrBr_3$ at a temperature of 516 K (in the presence of palladium black) resulted in hydrogen formation. Details of these experiments are given in reference 5. Use of this sequence in a practical cycle would depend on

increased reaction rates and more efficient use of the palladium catalyst.

A second halide hydrolysis sequence was also evaluated as a possible subcycle for HBr decomposition. The cycle is composed of reactions 9 and 10 in the following sequence.

9. $2CeOBr + 2H_2O = 2CeO_2 + 2HBr + H_2$

10. $2CeO_2 + 4HBr = 2CeOBr + 2H_2O + Br_2$

11. $2CeOBr + 4HBr = 2CeBr_3 + 2H_2O$

Reaction 10, conducted at temperatures between 775 and 875 K produced a solid CeOBr phase and bromine. Reaction 9, the hydrogen releasing reaction, was studied at temperatures from 1070-1250 K in order to obtain equilibrium data as well as kinetics. In these experiments measured quantities of H_2O were passed over CeOBr at the reaction temperature and the rate of hydrogen evolution was determined. Values of log K_p ranging from -5.5 to -3.0 were obtained over the temperature range investigated.(5) The ΔH^0 for the cerium oxybromide hydrolysis was found to be in the + 250 kJ region. At practical reaction temperatures, this set of reactions for HBr decomposition exhibits a positive ΔG^0 value. Thus they constitute a "hybrid" cycle for HBr decomposition in which mechanical work is used in the place of electrical work in the more familiar electrochemical-thermochemical hybrid cycle. The total positive ΔG^0 requirement will be reduced by an important $\Delta T \cdot \Delta S^0$ term, however, and will be significantly lower than the room temperature ΔG^0 for HBr decomposition.

Despite the above, a successful HBr sub-cycle has not yet been achieved, work with other compounds is continuing.

Use of Metal Sulfates in the H_2SO_4 Cycles

In the H_2SO_4 hybrid cycle (reactions (12-14) large amounts of heat are needed to dehydrate the sulfuric acid for the acid concentrations currently

12. $SO_2 + 2H_2O = H_2SO_4$ (aq.) $+ H_2$,

   electrochemical

13. H_2SO_4 (aq.) $= SO_3 + H_2O$

14. $SO_3 = SO_2 + 1/2O_2$
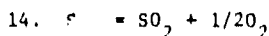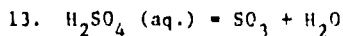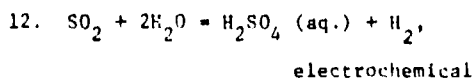
produced reaction 12. A significant saving in energy might be achieved by forming a suitable metal sulfate from the H_2SO_4. The alternative hybrid cycle may be represented by

12. $SO_2 + 2H_2O = H_2SO_4$ (aq.) $+ H_2$,

   electrochemical

12a. $H_2SO_4 + MO = MSO_4 + H_2O$

13a. $MSO_4 = MO + SO_3$

14. $SO_3 = SO_2 + 1/2O_2$
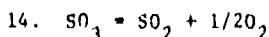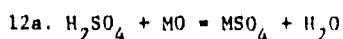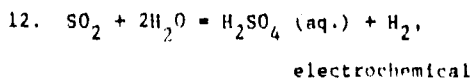
The same is true for the $H_2SO_4 - I_2$ cycle (reactions 15-17

15. $2H_2O + SO_2 + x I_2 = H_2SO_4 + 2HI_x$ (aq.)

2

16. $H_2SO_4 = H_2O + SO_2 + 1/2O_2$

17. $2HI_x = x\ I_2 + H_2$
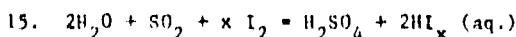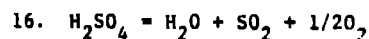
in which sulfuric acid produced in reaction 15 and phase separated from HI_x is dehydrated prior to thermal decomposition. The sulfate should have low solubility and form an anhydrous sulfate. An oxide sulfate may replace metal oxide in reaction 12. A survey and assessment of the literature were made for antimony and bismuth, both of which satisfy the first two criteria.

18. $Bi_2O_3 \cdot 3SO_3 = Bi_2O_3 \cdot 2SO_3 + SO_3$

19. $Bi_2O_3 \cdot 2SO_3 = Bi_2O_3 \cdot SO_3 + SO_3$

$Bi_2O_3 \cdot 3SO_3$ decomposes with increasing temperature to SO_3 and a series of oxide sulfates terminating in Bi_2O_3 itself. The equilibrium SO_3 pressure for reaction 18 is 1 atm at 860 K, and for reaction 19 is 1 atm at 1050 K. Final decomposition to form Bi_2O_3 occurs at higher temperatures. The options for generating SO_3 over a temperature range that includes intermediate temperatures (in addition to the high temperatures for SO_3 decomposition in reaction 14 should be useful in achieving efficient extraction of heat from the circulating helium gas of a high-temperature gas-cooled nuclear reactor. Experiments are being run to measure SO_3 pressure in the $Bi_2O_3 \cdot SO_3$ system.

Additional experiments are being carried out to obtain equilibrium concentrations and rates of reactions for bismuth oxide and bismuth oxysulfate with $\sim$ 50 wt% sulfuric acid solutions.

A preliminary evaluation of the energy efficiency of the bismuth sulfate alternate to the hybrid sulfuric acid cycle has been completed. The hybrid cycle has been described in the literature. (8) A process sensitivity study (9) using a simplified flow sheet seen in Fig. 1 illustrated the action of process variables on the cycle's efficiency. Data taken from this study were used as a basis for comparison with the modified process involving an insoluble bismuth sulfate. The flow sheet for this latter case is seen in Fig. 2. The sulfuric acid stream leaving the electrolyzer was assumed to be at 50 wt% concentration in both cases. An equilibrium yield of 75% was calculated for sulfur trioxide decomposition at 1100 K based on published thermodynamic data (JANAF Tables).

Tables III and IV illustrate the potential benefits to be gained on adopting the bismuth sulfate method of solution concentration. Reduction in the heat requirements for the acid concentration step as well as for the acid decomposition step show a potential gain of 12% in efficiency.

Future Research

In the LASL hydrogen program, we will continue to test reactions in cycles that are potentially suitable for different heat-source temperatures that also appear reasonable from the point of view of thermochemistry. From our laboratory experience, it is increasingly apparent that the most attractive cycles are usually impractical because of slow reaction rates for the low-temperature steps.

One method of improving kinetics is to utilize solution chemistry for low-temperature steps. We

plan to examine more closely solution chemistry as a method for promoting otherwise attractive cycles. We also hope to identify and incorporate precipitation reactions in order to minimize solution-drying operations. We hope the use of solution reactions will also give added flexibility and lead to the discovery of cycles that are less corrosive.

The preparation of flowsheets, together with engineering design activities, is continuing for the modified sulfuric acid cycles. Irreversibility analysis is being applied to these problems as well as the problem of gas separations with support in this area being given to the DOE Thermochemical Review Committee under the direction of Dr. J. E. Funk.

Thermochemical cycles capable of utilizing heat at high temperatures (1500-1700 K) are being investigated. These cycles, containing two or three steps, and involving perhaps an oxide or a sulfate decomposition, may be a means of producing a synthetic fuel (hydrogen) from magnetic fusion energy. Scopeing studies and a few preliminary experiments are envisioned at this time. This work should also be applicable to high temperature heat derived from solar energy.

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TABLE I

HEAT BALANCE FOR THE SULFURIC-ACID HYDROGEN BROMIDE CYCLE

(Units = kJ/mol H_2)

Step	Heat Requirement	Heat Available
1. H_2SO_4 (l) Heating	47	
2. H_2SO_4 Vaporization	56	
3. H_2SO_4 (g) Heating	$\frac{64}{167}$	
4. H_2SO_4 Decomposition (1100 K)	231	
5. Products Cooling		96
6. $SO_3/SO_2/O_2$ Separation	126	
7. $SO_2/Br_2/H_2O$ Reaction		18*
8. HBr Decomposition	$\frac{73}{597}$ (Theor.)	114

*Heat not available for matching

TABLE II

ESTIMATED EFFICIENCIES FOR THE SULFURIC ACID-HYDROGEN BROMIDE CYCLE

Basis: (1,2,3,) x Heat of Reaction, HBr Decomposition

(Units = kJ/mol H_2)

$$\text{Efficiency}_1 = \frac{286}{524 + 73 - 114} = 0.59$$

$$\text{Efficiency}_2 = \frac{286}{524 + 2(73) - 114} = 0.51$$

$$\text{Efficiency}_3 = \frac{286}{524 + 3(73) - 114} = 0.43$$

TABLE III

HEAT BALANCE FOR HYBRID SULFURIC ACID CYCLE

(Units = kJ/mol H_2 Produced)

Step	Power (heat Eq.)	Heat Required	Heat Available
1. Electrolysis	42(126)		42[a]
2. Acid Vaporization		648	
3. Acid Heating		314	
4. Acid Decomposition		285	
5. Acid Cooling			305
6. Acid Condensation			402
7. Steam Condensation			264[a]
8. $SO_2/SO_3/O_2$ Separation	42(126)		
	84(252)	1247	707 306[a]

$$\text{Efficiency} = \frac{286}{252 + 1247 - 707} = 0.361$$

[a]Heat unavailable for matching.

TABLE IV

HEAT BALANCE FOR BISMUTH SULFATE MODIFIED HYBRID SULFURIC ACID CYCLE

(Units = kJ/mol H_2 Produced)

Step	Power (Heat Eq.)	Heat Required	Heat Available
1. Electrolysis	42(126)		42[a]
2. Bismuth Sulfate Formation			13-26[a]
3. Bismuth Sulfate Decomposition		167-251 (estimated)	
4. SO_3 Decomposition		96	
5. $SO_3/SO_2/O_2$ Separation	42(126)		
	84(252)	263-347	55-68[a]

$$\text{Efficiency} = \frac{286}{599} \text{ (max)} = 0.478$$

[a] Heat unavailable for matching.

Fig. 1
Hybrid sulfuric acid cycle (simplified flow sheet).

Fig. 2
Hybrid sulfuric acid cycle, bismuth sulfate modification.